Table 1 Metal ion loadings

Metal salt	Quantity bound (mmol of metal/ g of SNAPY)*	% of available NAPY complexed*
Copper (II) nitrate	0.46	28
Copper (II) chloride	0.81	49
Iron (III) chloride	0.95	58
Europium (III) nitrate	0.55	34
Nickel (II) nitrate	0.57	35

* 1 g SNAPY polymer beads contains 1.63 mmol NAPY. Computation made assuming a metal to NAPY ratio equal to unity. If more than one NAPY per metal is involved, this value would be markedly increased

ing infinite dilution of the metal ions. In the case of the polymer-bound nitrates, increased band intensities in the region of 1400–1000 cm^{-2} which are assigned to nitrate modes superimposed on the skeletal vibrations of the polymer are observed[12]. The intensities of these bands are observed to diminish proportionally as the nitrate salt loadings are reduced. The chloride complexes do not exhibit these bands.

Due to its ability to swell the polymer support reasonably well and to dissolve a large number of metal salts, ethyl acetate is a convenient solvent in which to study metal loading. The results of such studies (*Table 1*) demonstrate that SNAPY is capable of binding to a wide variety of metal ions. The amount of metal complexed per mol SNAPY beads (g polymer)$^{-1}$ is similar to that obtained using SDIPY[6]. Assuming that each metal ion is coordinated to one ligand, iron (III) chloride is found to occupy 58% of the NAPY residues in SNAPY compared with all of the BIPY residues in SDIPY[6]. This difference may result from the increased functionalization of SNAPY (22% compared with SDIPY (14%) which would allow more than one NAPY to coordinate to a single metal ion. It is also known that NAPY, which forms a four-membered ring on chelation, is a much weaker field ligand than DIPY, which forms a five-membered ring, and hence does not bind as strongly to metal ions[13]. With copper (II) nitrate and copper (II) chloride, NAPY forms 1:2 and 1:1 complexes respectively[14,15] The large difference in amount of loading observed for these two salts of copper(II) reflects the known coordination chemistry and supports the suggestion that the polymer is flexible enough to allow more than one NAPY group to coordinate to a metal ion.

References

1 Hodge, P. *Chem. Br.* 1978, **14**, 237
2 Hodgkin, J. H. *Chem. Ind., London* 1979, 153
3 Melby, L. R. *J. Am. Chem. Soc.* 1975, **97**, 4044
4 Carraher, Jr., C. E., Sheats, J. E. and Pittman, Jr. C. U. *'Organometallic Polymers'*, Academic Press, New York, 1978
5 Tsutsiu, M. and Ugo, R. *'Fundamental Research in Homogeneous Catalysis'*, Plenum Press, New York, 1977
6 Card, R. J. and Neckers, D. C. *J. Am. Chem. Soc.* 1977, **99**, 7733
7 Hamada, Y. and Takeuchi, I. *Chem. Pharm. Bull.* 1971, **19**, 1857
8 Fuller, M. F. and Griffiths, P. R. *Anal. Chem.* 1978, **50**, 1906
9 Farrall, M. J. and Fréchet, J. M. J. *J. Org. Chem.* 1976, **41**, 3877
10 Armarego, W. L. F., Barlin, G. B. and Spinner, E. *Spectrochim. Acta* 1966, **20**, 117
11 Fuller, M. F. and Griffiths, P. R. *Am. Lab.* 1978, **10**, 69
12 Foster, R.J. and Hendricker, D. G. *Inorg. Chim. Acta* 1972, **6**, 371
13 Bodner, R. L. and Hendricker, D. G. *Inorg. Chem.* 1973, **12**, 33
14 Emerson, K., Emad, A., Brookes, R. W. and Martin, R. L. *Inorg. Chem.* 1973, **12**, 978
15 Foster, R. J. and Hendricker, D. G. *Inorg. Chem.* 1973, **12**, 349

Graft polymerization from glass surfaces

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An area of debate in the field of reinforced and filled polymers is the nature and importance of adhesion between the phases. Simple theories predict differences between the mechanical properties of filled polymers having poor adhesion and those having perfect adhesion between the phases[1]. Variations in the properties of filled polymers have been attributed to differences in interfacial adhesion[2,3]. Organochlorosilanes are widely used to promote adhesion between the phases in glass-filled polymers[4]; these agents have one or more groups which condense with the silanol groups on the glass to give covalent bonds between the organic groups and the glass. Often the organic groups are unsaturated, polymerizable groups which may be incorporated into chains of the surrounding matrix when that polymer is prepared or cured with treated glass *in situ*. Such reactions rely on chance encounters of active radicals with the unsaturated groups on the glass surface, and quantitative control of such processes is inherently difficult.

Our approach is to study glass-filled polymers with a controlled interface by growing polymer chains, ideally of known molecular weight and number per unit area of the surface, from specific sites incorporated on the glass surface. This method should provide positive attachment of a known quantity of polymer to the glass. The polymer-coated glass can then be incorporated into a matrix of polymer, chemically identical with the chains attached to the glass. Interfacial adhesion will rely on entanglements between the chains in the matrix and the bound chains and will depend on the molecular weight and number of such chains per unit area of the interface.

In this preliminary communication we describe a process by which suitable reactive sites are introduced on to the surfaces of glass beads and are subsequently used, in an established reaction, to initiate polymerization of vinyl

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monomers. Evidence is presented to show that this procedure leads to the formation of polymer chains attached to the glass surface.

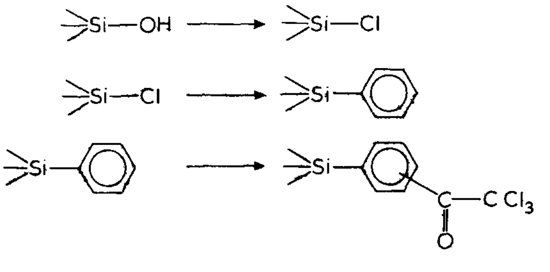
Experimental

Materials. Soda-lime glass beads (Potters–Ballotini Ltd.) of diameters 10–50 μm (average 30 μm, approx.) were used unfractionated after removing magnetic particles and cleaning by refluxing with propan-2-ol.

Chlorine 99%, sulphuryl chloride 97%, trichloracetic acid, trichloracetyl chloride, anhydrous aluminium chloride and silver cyanide (all from BDH Ltd), thionyl chloride (Hopkins & Williams Ltd), phenyl lithium (1.8 M solution in benzene–ether; Aldrich Chemicals Ltd), were used as supplied. Molybdenum carbonyl (BDH Ltd) was purified by vacuum sublimation. Styrene and methyl methacrylate were washed with sodium hydroxide solution to remove inhibitor and washed with distilled water. Styrene was dried over magnesium sulphate and methyl methacrylate over molecular sieve (Amberlite 4A). Both monomers were distilled under reduced pressure, stored under vacuum over calcium hydride and vacuum distilled immediately before use.

Instruments. Gas chromatograms were obtained with a Pye–Unicam Series 104 Chromatograph using 5% OV-1 on Chromosorb-G columns and helium carrier gas. Infrared spectra of surfaces were obtained using a Perkin–Elmer 257 spectrometer in conjunction with a Beckman TR-25 multiple *ATR* unit fitted with a KRS-5 crystal. A Cambridge Mk III Stereoscan was used to obtain scanning electron micrographs of surfaces of beads.

Incorporation of reactive sites onto glass surfaces. The initiation process adopted in a later part of this work requires reactive halogen and experience has shown that trichloroacetyl groups are suitable. We have developed a three-stage process, summarized in equations (1), to attach trichloroacetyl groups to glass surfaces.



(1a)

(1b)

(1c)

Chlorination. Direct reaction with hot chlorine gas was used in reaction (1a)[5]. Glass beads were reacted with chlorine in a tubular pyrex vessel fitted with a stopcock at each end and located in a tube-furnace. Chlorine, dried with concentrated sulphuric acid, was preheated in a glass coil. Residual gases leaving the furnace were cooled and passed into two traps containing concentrated sodium hydroxide solution and methyl red indicator; the first trap contained sufficient sodium hydroxide to absorb roughly 50 times the estimated amount of chlorine required to give complete reaction on the glass.

The furnace was preheated to 400°C under nitrogen which was replaced by a slow flow of chlorine gas. The chlorine flow was maintained until the indicator in the first trap was decolourized (about 1 h), when the chlorine was replaced by nitrogen while the furnace cooled. Finally, the stopcocks on the reaction tube were closed.

Prior to adopting the above technique both thionyl and sulphuryl chlorides were used as chlorinating agents, as described by other workers[6–8]. Although these reagents undoubtedly chlorinated the silanol groups, the products were contaminated with sulphur residues which were difficult to remove and which probably had adverse effects on subsequent processes, e.g. the polymerization reaction.

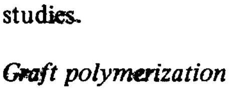
Phenylation. Phenylation of the chlorinated beads, reaction (1b), was achieved using a solution of lithium phenyl in benzene–ether (70:30 v/v). The reaction tube containing chlorinated beads was positioned vertically. Lithiumphenyl solution was introduced and allowed to percolate through the beads. Excess reagent was removed by eluting repeatedly with anhydrous ether. Lithium chloride was removed using dry methanol as eluent. The phenylated beads were transferred to a beaker, washed by decantation with dry methanol and dried under reduced pressure at 110°C.

Acylation. Trichloroacetyl groups were introduced, reaction (1c), by refluxing the phenylated beads with trichloroacetyl chloride and aluminium chloride for 1 h. Subsequently, the 'treated' beads were washed repeatedly with dry dichloromethane and freshly distilled methanol (to remove aluminium chloride) and were dried under reduced pressure at 110°C.

Freshly-prepared, treated beads (products of reaction 1c) were hydrophobic but lost this property after immersion in water for 1 day. Consequently, the treated beads were stored in a dry-box.

Alternative procedure. Beachell[9] has described the replacement of chlorine in chlorosilanes by nitrile groups according to reaction (2a). We adopted this approach to introduce nitrile groups onto the surface of glass beads. Chlorinated beads were refluxed for 15 h in a 0.2% (w/v) solution of silver cyanide in dry acetonitrile, washed repeatedly by decantation with warm acetonitrile and subsequently with warm dichloromethane. Nitrile groups were converted to amido groups, reaction (2b), by refluxing the beads with trichloroacetic acid in chloroform for 1 h. The beads were washed with chloroform and dried under vacuum at 80°C:

$$\equiv\mathrm{Si{-}Cl} + \mathrm{AgCN} \longrightarrow \equiv\mathrm{Si{-}CN} + \mathrm{AgCl} \qquad (2a)$$



$$\equiv\mathrm{Si{-}CN} + \mathrm{Cl_3CCOOH} \longrightarrow \equiv\mathrm{Si}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{N}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\mathrm{CCl_3}$$

(2b)

Subsequent polymerization reactions (performed as described later) established that this procedure was successful in incorporating trichloro groups. However, because of the difficulty of removing traces of unreacted silver cyanide and the relative lability of the Si–CO– grouping, the procedure described by scheme (1) was adopted for our major studies.

Graft polymerization

General aspects. The essential reactions leading to radical formation in the thermal (80°C) reaction between molybdenum carbonyl and reactive organic halides are[10,11]:

$$\mathrm{Mo(CO)_6} + \mathrm{S} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{(\mathrm{I})}{\mathrm{S{-}{-}{-}Mo(CO)_5}} + \mathrm{CO} \qquad (3a)$$

$$\mathrm{I} \xrightarrow{k_2'} \text{inactive products} \qquad (3b)$$

Table 1 Graft polymerizations using styrene monomer

Expt. No.	Glass bead sample	Temp. (°C)	Reaction time (h)	10^3 $[Mo(CO)_6]_0$ (mol l^{-1})	Ethyl acetate % (v/v)	Polymer on glass (% w/w)	Polymer thickness (μm)
1	A	80	18	28	0	0.50	0.060
2	A	80	45	39	50	0.24	0.029
3	B	80	16	39	50	0.46	0.055
4	C	80	18	39	50	0.64	0.077
5	C	80	19	0.17	50	0.39	0.047
6	C	70	16	0.17	50	0.18	0.022

Table 2 Graft polymerizations using methyl methacrylate monomer

Expt. No.	Temp. (°C)	Reaction time (min)	Polymer on glass (% w/w)	Polymer thickness (μm)
7	80	25	0.58	0.061
8	80	50	2.61	0.276
9	80	100	3.81	0.405
10	75	79	2.45	0.259
11	70	125	2.01	0.213

All polymerizations were carried out on glass beads sample C with $[Mo(CO)_6]_0 = 1.25 \times 10^{-3}$ mol l^{-1}

$$\mathrm{I} + \mathrm{R{-}Cl} \xrightarrow{k_3} \mathrm{Mo^{I}Cl} + \mathrm{R\cdot} \qquad (3c)$$

$$\mathrm{Mo^{I}Cl} + n\mathrm{R{-}Cl} \longrightarrow \mathrm{Mo^{V}} + \mathrm{SR\cdot} \qquad (3d)$$

where S is a donor solvent and may be monomer. Radicals R· initiate polymerization when the reaction is performed in the presence of a suitable monomer. We have established[12] that if the halide is of the form $R'{-}CCl_3$ reaction (3c) produces, exclusively, the radical $R'{-}\dot{C}Cl_2$. The specificity of (3c) ensures that, in the absence of chain transfer and thermal initiation, all polymer chains have end-groups derived from the organic group. In the present context R' represents glass with its attached groups. Assuming scheme (3) applies in the current experiments, primary chains should be attached to the glass through covalent bonds, as shown in *Figure 1*.

The detailed kinetics of scheme (3), established for a number of homogeneous polymerizations, are, in some measure, inapplicable in the present heterogeneous systems. Polymerizations in the presence of glass beads were performed under vacuum without stirring, using a greater volume of molybdenum carbonyl solution in monomer than was required to fill the voids between the beads. Radical formation through (3) was thus restricted to irregular voids with the halide component located on their surfaces. Diffusion of (I) to the glass surfaces should not seriously impede reaction (3c) before (1) decayed through (3b) since in methyl methacrylate polymerizations k'_2, k_3 have been estimated[13] as 2.4×10^{-3} s^{-1} and ~0.1 mol^{-1} l s^{-1}, respectively, and the dimensions of the voids are small.

Polymerizations. Conditions employed for preliminary graft polymerizations, using styrene (St) and methyl methacrylate (MMA) as monomers, are given in *Tables 1* and *2*, respectively; reaction mixtures were prepared in a dry-box and polymerizations were performed under high vacuum. After polymerization, the products were mixed with a large volume of solvent for the appropriate polymer [dichloromethane for polystyrene (PSt) and ethyl acetate for poly(methyl methacrylate) (PMMA)], to dissolve unbound polymer, monomer and initiator. The beads were isolated by decantation and the procedure repeated until all soluble polymer was removed. The beads, with any bound polymer, were dried under vacuum at 110°C.

Glass bead samples, A, B were prepared in the early stages when chlorination (1a) was achieved by refluxing with thionyl chloride; subsequent acylation was carried out as described above. Most St polymerizations were performed in the presence of ethyl acetate since studies in homogeneous solution have shown that the value of k_1 (reaction 3a) and, hence, the rate of initiation is greater if S is ethyl acetate or MMA[14], reaction times were sufficient to ensure complete reaction of $Mo(CO)_6$.

In principle, any labile halogen could react according to scheme (3) including the chlorine atoms attached to the glass surfaces in reaction (1a). Attempts to grow grafts of PSt from such beads, using $Mo(CO)_6$, resulted in vigorous and uncontrolled polymerizations when the reagents were mixed; reactions with MMA were less vigorous. While such reactions might produce grafted chains their study was not persued since it would be difficult to control the nature of the products.

EVIDENCE FOR GRAFT POLYMERIZATION

If graft polymerization from modified glass surfaces proceeds as envisaged, the product should be glass beads with an extremely thin ('monomolecular') layer of attached polymer chains. The yield of such grafts cannot be determined directly from monomer conversion.

After isolation, grafted beads adhered to each other strongly while ungrafted beads showed no adhesion. Grafted beads dispersed readily in the presence of a solvent for the appropriate polymer and adhered again when the solvent was removed. No adhesion was observed if polymerizations were performed either using azobisisobutyronitrile (AIBN) as initiator in the presence of untreated beads or by heating treated beads in monomer in the absence of $Mo(CO)_6$. The adhesion, which presumably arises from entanglements between chains on adjacent beads, provides good indirect evidence for the formation of grafted chains.

Gravimetric measurements

Quantities of polymer permanently associated with grafted beads were estimated gravimetrically by pyrolysing samples of dry, washed beads in air at 400°C for 1 h; more prolonged heating caused no additional weight loss. Pyrolysis cleaned, non-grafted beads lost no more than 0.1%

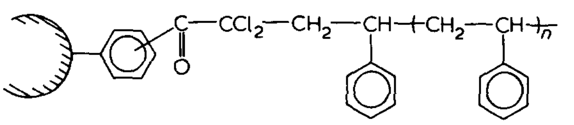


Figure 1 Mode of attachment of polystyrene chains to glass surface

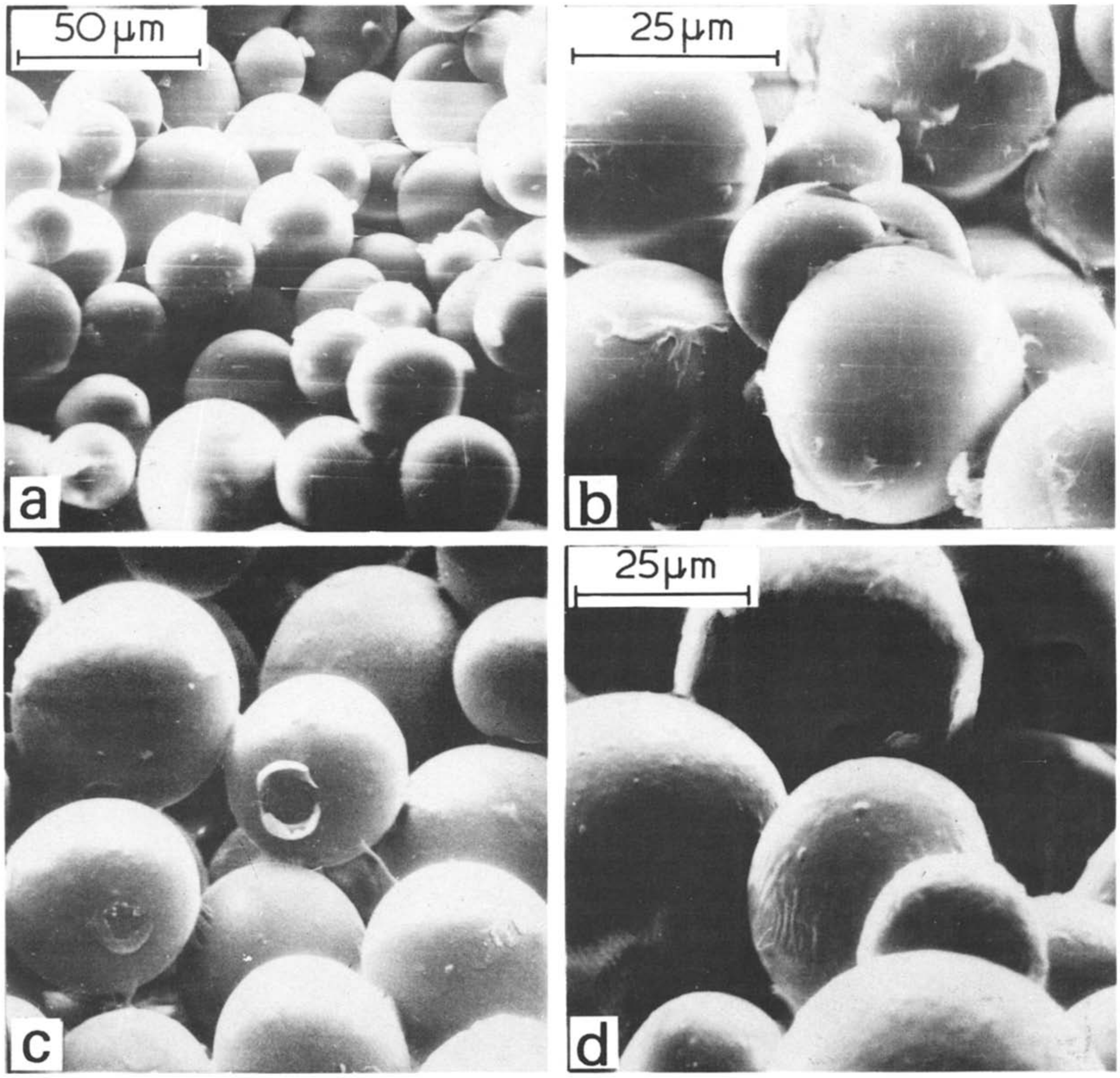


Figure 2 Scanning electron micrographs of various samples of glass beads: (a) after treatment to introduce reactive groups; (b) PSt-grafted beads from Expt. 1 (*Table 2*); (c) PMMA-grafted beads from Expt. 9 (*Table 2*), after evaporation of solvent; (d) as (c) but after swelling polymer in dichloromethane and pouring into methanol

of their original weight and no additional weight loss was observed if washed beads from AIBN initiated polymerizations were pyrolysed. The quantities of polymer associated with the glass, quoted in *Tables 1* and *2*, are not corrected for weight loss from untreated beads. These data provide strong evidence for the formation of polymer grafts on the surfaces of treated beads when reacted as described above. The relative amounts of attached PMMA and PSt are commensurate with the relative rate coefficients for propagation in the free-radical polymerizations of MMA and St at the same temperature.

Thicknesses of polymer coatings on grafted beads (*Tables 1* and *2*) were calculated from pyrolysis data assuming a uniformly thick layer on beads of diameter 30 µm; densities of glass, PSt and PMMA were taken as 2.5, 1.04, 1.19 g cm^{-3}, respectively. The calculated thicknesses are consistent with a single layer of polymer chains on the bead surfaces, especially if the number of attached chains per unit area of the interface is high. If a fraction of the total weight loss on pyrolysis of grafted beads did not arise from polymer but from the glass itself, and if this fraction corresponded to 0.1% of the weight of ungrafted beads, the thicknesses of PSt and PMMA layers should be reduced by 12 and 11 nm, approximately, respectively.

Degradation studies. Samples of PSt homopolymer and St-grafted beads (from Expt. 3, *Table 1*) were degraded (in capilliaries sealed under vacuum) at 400°C for one day and the products were subjected to gas chromatography. Chromatograms from different samples showed identical retention times for all significant peaks. Relative peak intensities were reproducible for a given material but some minor differences between chromatograms from homopolymer and grafted beads were noted; the origin of these variations has not been established. These experiments show qualitatively the presence of PSt on the surface of St-grafted beads. Attempts to make quantitative estimates of grafted polymer in this way, using PSt as standard, gave values of 0.35 to 1.1% (w/w) for one sample, compared with 0.46% (w/w) obtained gravimetrically.

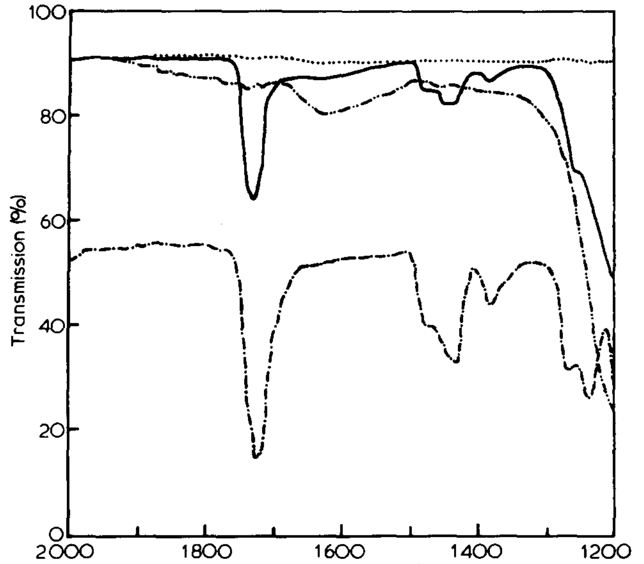


Figure 3 Infra-red *ATR* spectra on KRS-5 crystal (· · · ·), untreated glass (— · · — · ·), PMMA (— · — ·) and PMMA-grafted beads (———); angle of incidence 45°

Scanning electron microscopy. In *Figure 2a*, a scanning electron micrograph of beads subjected to reactions of scheme (1) (chlorinated by refluxing with thionyl chloride) shows a collection of beads having smooth surfaces and no adhesion between beads in contact. *Figures 2b* and *2c* show, respectively, PSt- and PMMA-grafted beads isolated by evaporation of solvent for the appropriate polymer. Apart from small irregular and isolated islands of surface material these beads also exhibit generally smooth surfaces but with some evidence of adhesive material. The islands are too small to account for the surface polymer estimated gravimetrically. The micrographs are consistent with an essentially uniform layer of grafted polymer and we propose that the islands are fracture surfaces from regions where spheres have come into contact during isolation and the grafted chains have entangled.

Figure 2d was obtained from a sample of PMMA-grafted beads treated with dichloromethane, to swell the grafts, and poured into methanol, to precipitate the grafts. Instead of a smooth surface produced by solvent evaporation these beads exhibit a wrinkled surface. This modification of surface features is further evidence for the existence of grafted chains and good surface coverage.

Infra-red spectroscopy and polymerization on glass slides. Detection of an essentially monomolecular layer of polymer on the surfaces of small beads is not readily achieved by conventional spectroscopic techniques. We attempted to obtain infra-red spectra of surface layers using a total reflection accessory providing about 25 reflections on the sample surface. With dry PSt-grafted beads we observed absorptions at 2825–2960, 1450 and 700 cm^{-1}, characteristic of PSt, and an absorption at 1730 cm^{-1} which may have arisen from unreacted trichloroacetyl groups; the pressure required to provide adequate contact between the beads and the accessory crystal damaged the crystal permanently. As an alternative procedure we deposited a suspension of PMMA-grafted beads in dichloromethane on the crystal and removed the solvent. Characteristic absorptions of PMMA at 1725, 1440, 1230, 1190 and 1140 cm^{-1} were obtained but the absorptions were weak.

To obtain better contact between sample and crystal we subjected glass microscope slides to the same chemical treatment as the beads, grafting them with PMMA; *ATR* spectra were obtained for untreated slides, grafted slides and for PMMA homopolymer. Using an angle of incidence of 45°, the spectra, shown in *Figure 3*, provide evidence for a PMMA layer on the grafted slides. Variations in the intensities of the absorption peaks with angle of incidence were consistent with a polymer layer ~0.5 μm thick.

Further evidence for a layer of polymer on grafted slides was obtained by immersing them in an ethyl acetate solution of Waxoline Red O dye for several hours. The slides were removed from the solution and the solvent was evaporated. Superficial dye was removed by washing the slides with methanol. Comparisons showed that considerably more dye was retained on grafted than on ungrafted slides.

POLYMERIZATION KINETICS

As indicated earlier, the kinetics of grafting from beads are complex, involving diffusion of active species to the glass surface and restriction of subsequent polymerization to the vicinity of that surface. We have performed a few preliminary kinetic experiments, reacting trichloroacetylated glass beads in 50:50 (v/v) styrene–ethyl acetate solutions of $Mo(CO)_6$ at 80°C for 5 h; percentage weight losses on pyrolysis of the beads are presented in *Figure 4*. Assuming that only ethyl acetate is reactive in (3a) the half-life of $Mo(CO)_6$ under these conditions is approximately 3.8 h[14]. In homogeneous systems we would expect secondary radical formation, through (3d), to play little part in forming initiating radicals[11]. Under present conditions this expectation may not apply since the Mo^I species involved in (3d) are formed, in (3c), in a region of high halide concentration.

It is apparent, from *Figure 4*, that optimum conditions exist for maximizing the formation of graft polymer on glass surfaces. From these limited data it is unrealistic to derive a detailed mechanism. However, we suggest, in outline, a tentative mechanism to account for these data. At low $[Mo(CO)_6]$ rates of radical formation and the concentrations of propagating radicals attached to the glass surface will be low. By analogy with homogeneous polymerizations, we anticipate that degrees of polymerization of grafts will decrease as $[Mo(CO)_6]_0$ (the initial

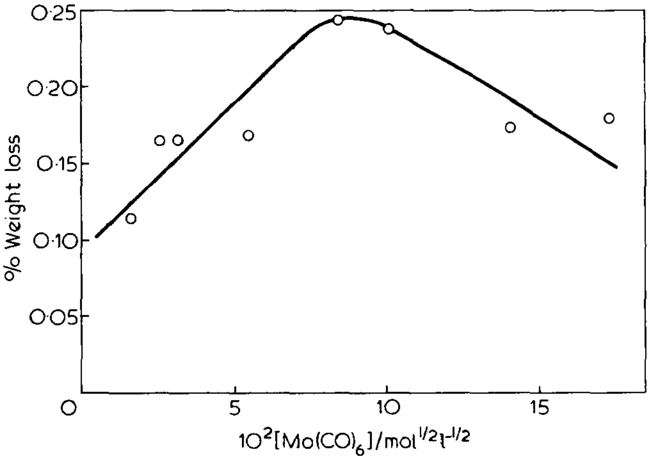


Figure 4 Percentage weight loss of PSt-grafted beads on pyrolysis as a function of $[Mo(CO)_6]_0$ in the polymerization reaction: graft polymerizations were performed in styrene–ethyl acetate solution (50:50 v/v) for 5 h at 80°C

concentration of $Mo(CO)_6$) increases, but that the number of chains formed will be proportional to $[Mo(CO)_6]_0$. Assuming the same dependence of chain length on rate of initiation as in homogeneous systems we predict that the yield of graft polymer will be proportional to $[Mo(CO)_6]_0^{1/2}$.

At high $[Mo(CO)_6]_0$ ($\sim 10^{-2}$ mol l^{-1}) rates of initiation will be high with high local concentrations of propagating radicals on the surfaces. Mutual termination of these radicals will result in comparatively short grafts. It is also likely that, under the reaction conditions employed, the surface will become effectively saturated with interpenetrating grafts forming a barrier to further reaction. Thus, a constant number of grafts may be formed. Their average length and, hence, the polymer yield will decrease with increasing $[Mo(CO)_6]_0$.

DISCUSSION

The analytical and spectroscopic data demonstrate that we have developed a successful method of incorporating on to glass surfaces reactive groups which can act as initiation sites for graft polymerization in the presence of molybdenum carbonyl and suitable monomer. Quantitative data and the results of electron microscopy are consistent with the formation of an essentially uniform 'monomolecular' layer of grafts on the glass surface.

Under the conditions of our experiments we expect approximately three hydroxyl groups per 1 nm^2 of the glass surface[15] to be available for chlorination. Assuming one third of these sites eventually become points of attachment of graft chains there would be, on average, about one junction point per 100 $Å^2$. For a polymer layer 0.25 μm thick (see *Table 2*), these conditions correspond to a degree of polymerization of about 1000 per graft site, which is a sensible kinetic chain length for free-radical polymerization. Because of the modes of bimolecular termination of propagating radicals[16] PMMA is expected to form mainly simple grafts while, depending on the extent of transfer and thermal initiation, a large proportion of the PSt chains are expected to be in the form of loops on the glass surface.

Currently, work is in progress to determine the numbers and lengths of the grafts and to develop reproducible methods of incorporating grafted beads into polymeric matrices where it is highly probable that at equilibrium the mixing of bound and unbound chains is unfavourable[17,18] Only then will it be possible to control the interfaces between grafted beads and a matrix.

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References

1 Nielsen, L. E. *J. Appl. Polym. Sci.*, 1966, **10**, 97
2 Morton, M., Murphy, R. J. and Cheng, T. C. in 'Copolymers, Polyblends and Composites' (Ed. N. A. J. Platzer) *Adv. Chem. Ser.* **142**, Am. Chem. Soc., 1975
3 Lewis, T. B. and Nielsen, L. E. *J. Appl. Polym. Sci.* 1970, **14**, 1449
4 For example, Kaas, R. L. and Kardos, J. L. *Polym. Eng. Sci.* 1971, **11**, 11
5 Hair, M. L. 'Infrared Spectroscopy in Surface Chemistry', Marcel Dekker, NY, 1967; Elmer, T. H. and Nordberg, M. E. Belg. Pat. 650,244 (1965)
6 Deuel, H., Wartmann, J., Hutschnecker, K., Scholinger, U. and Güdel, C. *Helv. Chim. Acta* 1959, **42**, 1160
7 Folman, M. *Trans. Faraday Soc.* 1967, **57**, 2000; Scherbakova and Slovetskaya, *Dokl. Akad. Sci. USSR* 1951, **111**, 855
8 Buslaev, G. S., Karitonov, N. P. and Platonova, V. I. *Izv. Akad. Nauk SSSR, Neorgan Materialy*, 1965, **1**, 1607
9 Beachell, H. C. *J. Am. Chem. Soc.* 1952, **74**, 5247
10 Bamford, C. H., Eastmond, G. C. and Maltman, W. R. *Trans. Faraday Soc.* 1966, **62**, 2531
11 Bamford, C. H., Eastmond, G. C. and Fildes, F. J. T. *Proc. Roy. Soc.*, 1972, **A326**, 431
12 Bamford, C. H., Dyson, R. W., Eastmond, G. C. and Whittle, D. *Polymer* 1964, **10**, 759
13 Bamford, C. H. and Sakamoto, I. *J. Chem. Soc. Faraday Trans. I* 1974, **70**, 344
14 Bamford, C. H., Denyer, R. and Eastmond, G. C. *Trans. Faraday Soc.* 1965, **61**, 1459
15 Dawson, J. B. Pilkington Bros. Ltd, private communication
16 Bamford, C. H., Dyson, R. W. and Eastmond, G. C. *Polymer* 1969, **10**, 885
17 Eastmond, G. C. and Phillips, D. G. in 'Polymer Alloys' (Eds. D. Klempner and K. C. Frisch) Plenum Press, NY 1977, 141; *Polymer* 1979, **20**, 1501
18 Meier, D. J. *Polym. Prepr.* 1977, **18**(1), 340

Kinetics of cure of epoxy resin system bisphenol-A diglycidylether-di(4-aminophenyl)sulphone

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Introduction

In this communication, the kinetics of cure of stoichiometric mixtures of the epoxy resin bisphenol-A diglycidylether, and the curing agent di(4-aminophenyl)sulphone, have been investigated by differential scanning calorimetry in the temperature range 140°–200°C. The results are described by a kinetic equation which accounts for the diffusion control of the curing reactions. It is assumed that the rate-determining step is the autocatalysed reaction of an epoxide–amine complex with hydrogen-bond donor molecules, such as species containing hydroxyl groups.

A common feature of many epoxy resin systems is that the curing process is autocatalytic in nature and is diffusion-controlled in its later stages. A quantitative description of the curing process should account for these phenomena.

A kinetic equation which has been used to describe the autocatalytic cure of various epoxy resin systems is of the form:

$$r = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (1)$$

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